LIQUID FUEL FROM BIO-MASS

Thesis submitted in partial fulfillment of the requirements for
The degree of

Master of Technology (R)

In

DEPARTMENT OF CHEMICAL ENGINEERING

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Certificate

This is to certify that the thesis entitled ***"liquid fuel from bio-mass"*** *by* ***Mr. Krushna Prasad Shadangi*** *submitted to the National Institute of Technology, Rourkela for the Degree of Master of Technology (R) is a record of bonafide research work, carried out by him in the Department of Chemical Engineering under my supervision. I believe that the thesis fulfils part of the requirements for the award of master of Technology. The results embodied in the thesis have not been submitted for the award of any other degree.*

Prof. (Dr). R.K Singh
Department of Chemical Engineering
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PREFACE OF THESIS

The thesis addresses production of liquid fuel from different oil containing seed by the process of thermal pyrolysis, carried out in a semi batch reactor. The thesis gives the idea about the production of liquid fuel from biomass, includes five chapters.

Chapter 1 shows the introduction to bio fuel, objective of the projective of the project, project need and justification and the utility of the project practically.

Chapter 2 devoted on the literature on bio-mass, types and sources of bio-mass, constituent of biomass, different methods of conversion of biomass to bio-fuel, factor affecting on the yield during the pyrolysis, types of pyrolysis, composition and the application of bio-fuel.

Chapter 3 includes the characterization of raw materials, methodology for the production of liquid fuel from the oil containing seeds, thermal behavior of the raw materials, characterization of the oil and chars, which includes the techniques used to find out the elemental composition, functional group presents and chemical composition in the pyrolytic products by different analytical instruments.

The results obtained from the experiment are summarized in chapter 4. It includes the discussion of experimental results as well as the interpretation of the reports of instrumental analysis using TGA, FTIR, GC-MS and SEM/EDX.

The conclusion to the production of liquid fuel from biomass is discussed in chapter 5.

ACKNOWLEDGEMENT

I take opportunity to express my gratitude to all those who motivated, encouraged and helped me in this project work. I am grateful to my supervisor *Prof. (Dr.) R.K. Singh*, for his kind support, guidance and encouragement throughout the project work, also for introducing to this topic, which has been very interesting and given me great insight to the future work on this area.

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ABSTRACT

Bio-energy is now accepted as having the potential to provide the major part of the projected renewable energy provisions of the future. Pyrolysis is one of the three main thermal routes, with gasification and combustion, for providing a useful and valuable bio-fuel. Thermal pyrolysis of castor seeds, soybean seeds and polanga de-oiled cake were carried out in a semi batch reactor made up of stainless steel at temperature range from 450^{o}C to 600^{o}C to produce bio-fuel. The effect of temperature on pyrolysis of the above raw materials is studied to know the optimum temperature for maximum liquid yield. The thermal degradation temperatures of the raw materials are studied using thermo gravimetric analysis (TGA) at a heating rate of 20^{o}C/min. in air atmosphere. The oil samples obtained at optimum condition is analyzed according to their fuel properties, elemental analysis, functional group presents, and compounds presents.

PRODUCTION OF LIQUID FUEL FROM BIOMASS

CHAPTER-1

(INTRODUCTION)

1. INTRODUCTION

Energy is essential for development and the demand for energy is increasing continuously due to the rapid outgrowth of population and urbanization. Present sources of energy are not sufficient to overcome the increasing needs. World energy demand is expected to increase approximately 50% above 2002 level and will increase approximately two and half times the present level. The major energy demand is fulfilled from the conventional energy resources like coal, petroleum and natural gas. These sources are in the verge of getting extinct. It was estimated that the oil sources might be depleted till 2050.

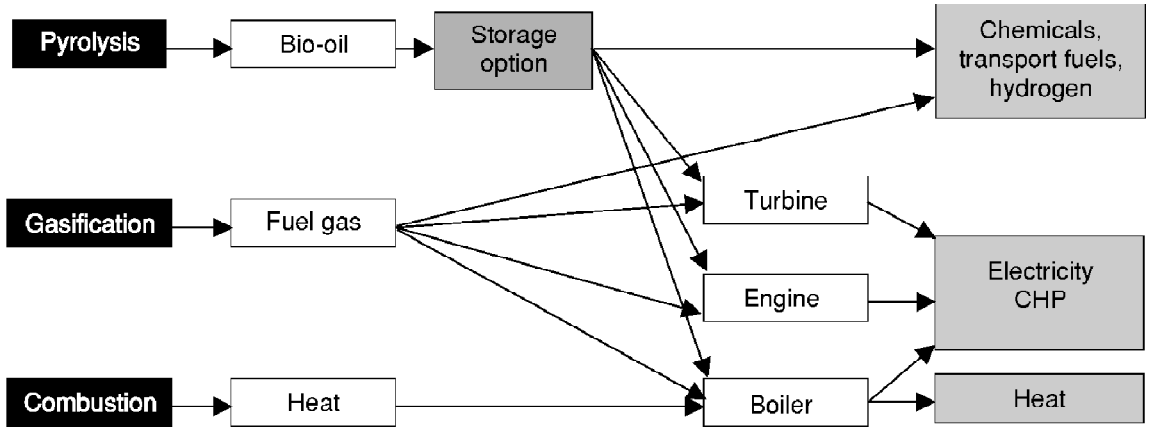
In view of the escalating energy (fuel) crisis and environmental degradation, bio-fuel is one of the sources for replacement of fossil fuel, thereby reducing country's dependence on importing crude petroleum from overseas country. The rising of the prices of petroleum fuels, depletion of oil reserves and stiff regulations on exhaust emissions have necessitated the substitution of fossil fuels with less polluting and easily available renewable fuels for use in internal combustion engines. Development of bio fuel as an alternative and renewable source of energy for the mechanized agricultural and transportation sector has become critical in the national effort towards maximum self-reliance for the corner stone of our energy security strategy. Bio-fuel is environment friendly and carbon dioxide neutral. The concept of using bio-fuel in diesel engines was originated from the demonstration of first diesel engine by the inventor of diesel engine ''Rudolf Diesel" at the World Exhibition at Paris in 1900 by using peanut oil as fuel. In the recent years, serious efforts have been made by several researchers to use different source of energy as fuel in existing diesel engines. The use of biomass as fuels for transportation, generating electricity and heat has become a focus of renewed interest in many parts of the world. Biomass is an indigenous, often cheap, and above all renewable fuel. The increasing availability of bio-mass combined with the recent development of technologies to use it

efficiently and with low level of emissions promises to make biomass an increasingly attractive fuel option. Biomass, in contrast to fossil fuels, has a unique potential for making a positive environmental impact. That is, in a plan for sustainable biomass production and use, the carbon dioxide (CO_2) emitted would be absorbed by the growth of new biomass.

The different processes such as thermo chemical and bio chemical process are used to convert biomass to fuel (fig. 1). Among these processes pyrolysis is one of the suitable thermo chemical conversion processes to get maximum liquid product from biomass. Any type of biomass can give liquid product after pyrolysis which can be used as fuel and also for production of different chemicals which is discussed in the 2nd chapter. Bio diesel has been introduced in many countries as fuels for transportation propose which is produced by transesterification of edible and non edible seed oils. In this process the oil produced by the cold pressing of different oil containing seeds is esterified in presence of different catalyst to get bio diesel. During the process of cold pressing, after extraction of oil from seed some amount of also remains in the de-oiled cake. So less amount of is extracted, which is again sent for transesterification purpose to produce bio diesel. But by the process of pyrolysis maximum liquid yield can be obtained from the seed directly.

Here work has been carried out on different seeds such as castor seed, soybean seed and polanga seed de-oiled cake to obtain fuel oil by the process of pyrolysis. The physical and chemical property of pyrolytic oil shows that, the oil has a positive affinity towards the use of oil as transportation purpose.

Fig 1: Thermo chemical conversion of bio mass



CHAPTER-2

(LIRETATURE SURVEY)

2. LITERATURE SURVEY

2.1 BIOMASS

Biomass refers to any organic materials that are derived from plants or animals. In general it is difficult to find out the actual definition. Biomass is non-fossilized and biodegradable organic material originating from plants, animals and micro-organisms. This includes the products, by-products, residues and wastes from agriculture, forestry, industrial and municipal wastes. Biomass also includes gases and liquids recovered from the decomposition of non fossilized and biodegradable organic materials. As a sustainable and renewable energy resource, biomass is constantly being formed by the interaction of CO_2, air, water, soil, and sunlight with plants and animals. When an organism dies, microorganisms break down into elementary constituent parts like H_2O, CO_2, and its potential energy. Because plants use the same the carbon dioxide at the time of photosynthesis, the amount of CO_2 does not increase in the earth. It is thus called greenhouse gas neutral or GHG neutral. It does not include organic materials that converted to coal or petroleum over many millions of years by geological processes. Biomass comes from botanical (plant species) or biological (animal waste or carcass) sources, or from a combination of these.

2.2 SOURCES OF BIOMASS

The Common sources of biomass are agricultural, forest, municipal and biological. The examples of sources are discussed below.

- Agricultural*:* food grain, bagasse (crushed sugarcane), corn stalks, straw, seed hulls, nutshells, and manure from cattle, poultry, and hogs.
- Forest: trees, wood waste, wood or bark, sawdust, timber slash, and mill scrap.

- Municipal: sewage sludge, refuse-derived fuel (RDF), food waste, waste paper, and yard clippings.
- Biological: animal waste, aquatic species, biological waste.

2.3 TYPES OF BIOMASS

The whole biomass is categorized in different groups such as fuel bio mass, feed biomass, organic fertilizer biomass, fiber biomass and chemical biomass according to their utility. Biomass may also be divided into two broad groups:

- Virgin biomass includes wood, plants, and leaves (ligno-cellulose); and crops and vegetables (carbohydrates).
- Waste includes solid and liquid wastes (municipal solid waste (MSW)); sewage, animal, and human waste; gases derived from land filling (mainly methane); and agricultural wastes.

Depending on the nature and availability, the bio wastes and organic residues can be utilized in different manners as described below. [1]

2.3.1 Fuel biomass

The biomass, used for production of energy is known as fuel biomass. There are three different forms of energy like solid, liquid and gaseous fuel, obtained from biomass. Biomass from plants and animal origin are directly burnt for cooking and other purposes. Municipal and sewage wastes, industrial wastes and agricultural wastes are converted to energy which can meet the demand for energy in rural sector. Paddy straw and rice husk can be profitably converted to fuel gas by thermal decomposition. Ethanol, which is used as a liquid fuel can be produced from carbohydrates by alcoholic fermentation. When wood and agricultural residues are heated in the absence of air (pyrolysis), charcoal is the resultant product which can be used as a fuel more

advantageously than wood. By the process of gasification, gas is evolved which can be used as a fuel for engines. Biogas, which is popular in rural areas, is produced by anaerobic fermentation from farm wastes.

2.3.2 Feed biomass

Conventionally, crop residues are used as cattle-feed. However, some of them with high percentage of lignin or non-digestible constituents need certain treatments such as soaking in water, alkali/alcohol to make their use as a fuel. The oil-cakes of various crop seed like cotton, rubber, tobacco etc. can also be used as a feed after extraction of toxic materials.

2.3.3 Organic fertilizer biomass

The biomass used as fertilizer to soil is known as fertilizer biomass. Dry fermented slurry can be used as a direct organic fertilizer for crop land.

2.3.4 Fiber biomass

The fibrous agricultural wastes and residues are being profitably utilized for making pulp for cheap grade paper.

2.3.5 Chemical biomass

Highly siliceous agricultural residues like rice husk and rice straw can be converted into useful chemicals like amorphous silicon, silicate products and solar grade silicon. Furfural is another chemical, can be produced from biogases, cotton seed hulls, corn-cobs, flax fibers, oat hulls etc., which is used as a solvent for some petroleum products.

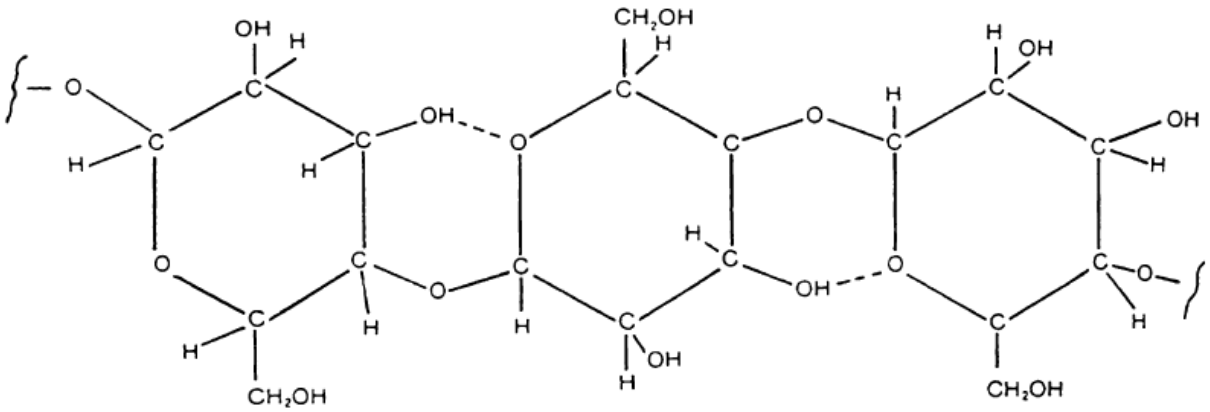
2.4 CONSTITUENTS OF BIOMASS

The major constituents of biomass are cellulose, hemicelluloses and lignin. [2]

1.4.1 Cellulose

The primary organic component of the cell wall of the biomass is cellulose. It is represented by generic formula $(C_6H_{10}O_5)$ n. Cellulose is of a crystalline, strong structure that is resistant to hydrolysis and a long chain polymer with a high degree of polymerization (~10,000) and a large molecular weight (~500,000). Cellulose is primarily composed of d-glucose, which is made of six carbons (fig. 2.1). Cellulose is highly insoluble and, though a carbohydrate is not digestible by humans. It is a dominant component of wood, making up about 40 to 44% by dry weight. Its amount varies from 90% (by weight) in cotton to 33% for most other plants.

Fig 2.1 Molecular structure of cellulose

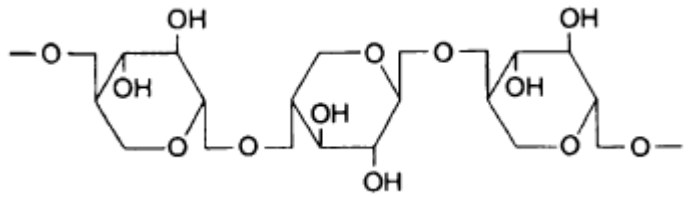


2.4.2 Hemicelluloses

The constituent of the cell wall of the plant is hemicelluloses and represented by the generic formula $(C_5H_8O_4)$ n. It is a group of carbohydrates with a branched chain structure and a lower degree of polymerization (~100–200) Fig. 2.2 shows the molecular arrangement of a typical hemicelluloses molecule, it constitutes about 20 to 30% of the dry weight of most wood. The composition and structure of hemicelluloses varies from biomass to biomass. Most of the

hemicelluloses contain some simple sugar residues like D-xylose (the most common), D-glucose, D-galactose, D-ababinose, D-glucurnoic acid, and D-mannose. These typically contain 50 to 200 units in their branched structures. It is soluble in weak alkaline solutions and is easily hydrolyzed by dilute acid or base. The presence of hemicelluloses yields more gases and less tar than cellulose at the time of decomposition.

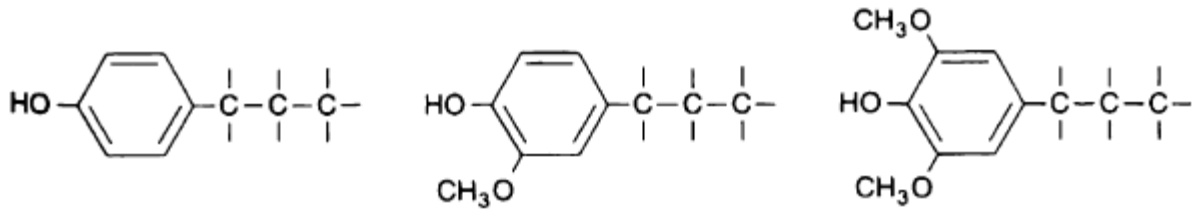
Fig 2.2 Molecular structure of typical hemicelluloses



2.4.3 Lignin

The third important constituent of woody biomass is lignin, which is complex in nature, highly branch polymer of phenyl propane and is an integral part of the secondary cell walls of plants. It is primarily a three dimensional polymer of 4-propenyl phenol, 4-propenyl-2-methoxy phenol, and 4-propenyl-2.5-dimethoxyl phenol. It is one of the most abundant organic polymers on Earth (exceeded only by cellulose). Lignin is the cementing agent for cellulose fibers holding adjacent cells together. The dominant monomeric units in the polymers are benzene rings. Fig. 3 shows some structure of lignin, which is composed primarily of lignin, glues together adjacent cells. Lignin is highly insoluble, even in sulphuric acid. A typical hardwood contains about 18 to 25%, while softwood contains 25 to 35% by dry weight.

Fig. 2.3 Structural units of lignin



2.5 BIO FUEL

Bio-fuels are produced from living organisms or from metabolic by-products (organic or food waste products). In order to be considered a bio-fuel the fuel must contain over 80 percent renewable materials. It is originally derived from the photosynthesis process and can therefore often be referred as a source of solar energy. The term bio fuel covers solid biomass, liquid fuels and gaseous fuel. Solid bio-fuel includes wood, sawdust, grass cuttings, domestic refuse, charcoal, agricultural waste, non-food energy crops and dried manure where biodiesel, bio-alcohol, bio-ether, pyrolytic oil are liquid bio-fuel and syngas and bio gas are gaseous bio-fuel. [3]

2.6 METHODS OF THERMAL CONVERSION OF BIOMASS TO BIO-FUEL

Biomass can be converted into solid, liquid and gaseous fuels by a number of processes. The technologies include thermal, thermo-chemical and bio-chemical conversions. The actual processes in these technologies are combustion, pyrolysis, gasification, alcoholic fermentation, liquefaction etc. The main products of conversion technologies are energy (thermal, steam, electricity), solid fuels (charcoal, combustibles), synthetic fuels (methanol, methane, hydrogen gas etc.) and pyrolytic oil. These can be used for different purposes like cooking, lighting, heating, water pumping, electricity generation and as industrial and transport fuels. [4]

2.6.1 Combustion

Combustion or burning is process of conversion of biomass into energy, where the complete oxidation of carbon taking place to CO_2 and the results energy in the form of heat. It is an exothermic chemical reaction between fuel and oxidant. It includes direct burning of dried wood, cow dunk cake, burning of bagasse in boilers and results heat energy. In a complete combustion reaction, a compound reacts with an oxidizing element, such as oxygen or fluorine, and the products are compounds of each element in the fuel with the oxidizing element. For example:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{energy}$$

$$CH_2S + 6F_2 \rightarrow CF_4 + 2HF + SF_6$$

In general complete combustion is almost impossible to achieve. In reality, as actual combustion reactions come to equilibrium, a wide variety of major and minor species will be present such as carbon monoxide and pure carbon (soot or ash). Additionally, any combustion in air, which is 78% nitrogen, will also create several forms of nitrogen oxides. This is the easy method to get energy from biomass. Now this method is also used to get energy from biomass but one of the drawbacks of this process is that the thermal efficiency is very low and emission related problems. [5]

2.6.2 Gasification

Gasification is the conversion, by partial oxidation at high temperature; of a carbonaceous feed stock into a gaseous fuel. The heating value of the resulting gases generally ranges from about one tenth to half that of natural gas, depending on the gasification process used. The product gas can be used in the production of heat, electricity by direct firing in the engine and boiler after suitable clean up. Alternatively the produced gas is used to produce fuel like methanol, and

hydrogen which can be used in the fuel cell. Gasification of biomass has more advantages than combustion in the terms of economics of scale and clean and efficient operation. In the process of gasification the biomass materials goes in different steps. The first step of gasification is pyrolysis, where carbonaceous particle heats up and Volatiles are released and char is produced. In the second step combustion process occurs as the volatile products and some of the char reacts with oxygen to form carbon dioxide and carbon monoxide, which provides heat for the subsequent gasification reactions. For example: $C + \frac{1}{2}O_2 \rightarrow CO$. In the third step gasification occurs as the char reacts with carbon dioxide and steam to produce carbon monoxide and hydrogen, via the reaction $C + H_2O \rightarrow H_2 + CO$. In addition, the reversible gas phase water gas shift reaction reaches equilibrium very fast at the temperatures in a gasifier. This balances the concentrations of carbon monoxide, steam, carbon dioxide and hydrogen. $CO + H_2O \leftrightarrow CO_2 + H_2$ Gasification also produces methane, which can be burned directly for energy production. Gasification is carried out generally in one of the three major types of gasifier:

- Moving bed
- Fluidized bed
- Entrained flow

Downdraft and updraft are two common types of moving-bed gasifier. A survey of gasifiers in Europe, the United States, and Canada shows that downdraft gasifiers are the most common. It shows that 75% are downdraft, 20% are fluidized beds, 2.5% are updraft, and 2.5% are of various other designs.

2.6.3 Liquefaction

Liquefaction is a process of conversion of biomass into bio fuel and chemicals where conversion takes place in presence of solvent and catalyst at 350^{o}C temperature and 12-20 MPa pressure. The solvent may be phenol, glycerol, and water in nitrogen or hydrogen atmosphere. Alkali may be added to promote organic conversion. The primary product is organic liquid with reduce oxygen content. The nature of these compounds was found to be dependent on the catalyst, but not appreciably on the physical conditions used. [7]

2.6.4 Alcoholic fermentation

Alcoholic fermentation, is a biological process in which sugars such as glucose, fructose, and sucrose are converted into cellular energy and thereby produce ethanol and carbon dioxide as metabolic waste products. The feed stocks for this process are simple sugar, baggase and other plants which store the energy as more complex sugar like starch, cellulosic biomass that is made of very complex sugar polymers etc. During hydrolysis, acids and catalysts ate used to catalyze the reaction. The sugar is converted into ethanol in presence of bacteria or yeast in absence of oxygen. So it is classified as anaerobic. In case of fermentation process, one glucose molecule is converted into two ethanol molecules and two carbon dioxide molecules:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

Before fermentation takes place, one glucose molecule is broken down into two private molecules. This is known as glycolysis.[1] Glycolysis is summarized by the chemical equation:

$$C_6H_{12}O_6 + 2\ ADP + 2\ P_i + 2\ NAD^+ \rightarrow 2\ CH_3COCOO^- + 2\ ATP + 2\ NADH + 2\ H_2O + 2H^+$$

As shown by the reaction equation, glycolysis causes the reduction of two molecules of Nicotinamide adenine dinucleotide to two Adenosine diphosphate molecules are also converted

to two Adenosine-5'-triphosphate and two water molecules via substrate-level phosphorylation. [8-10]

2.6.5 Pyrolysis

Pyrolysis is one of the best methods to convert all biomass materials into bio oil, char and volatiles. Pyrolysis is the process of heating of organic materials the absence of air or oxygen at high temperature of 500 – 1100^{o}C. The bio oil obtained by this process contains 10-20% water [11]. Bio-oil is produced by rapidly and simultaneously depolymerizing and fragmenting the cellulose, hemicelluloses, and lignin components of biomass. In a typical operation, the biomass is subjected to a rapid increase in temperature followed by an immediate quenching to "freeze" the intermediate pyrolytic products. Rapid quenching is important, as it prevents further degradation, cleavage, or reaction with other. Bio-oil is a micro emulsion, in which the continuous phase is an aqueous solution of the products of cellulose and hemicelluloses decomposition, and small molecules from lignin decomposition. The discontinuous phase is largely composed of pyrolytic lignin macromolecules [12]. The bio oil can be used as fuel for transportation purpose. The compounds presents in bio-oil fall into the following five broad categories. [11] They are:

- Hydroxyaldehydes
- Hydroxyketones
- Sugars and dehydrosugars
- Carboxylic acids
- Phenolic compounds

The nature of the product depends on several factors, including pyrolysis temperature and heating rate and catalyst. The condensable gas may break down further into noncondensable gases (CO, CO_2, H_2, and CH_4), liquid, and char. This decomposition occurs partly through gas-phase homogeneous reactions and partly through gas-solid-phase heterogeneous thermal reactions. In gas-phase reactions, the condensable vapor is cracked into smaller molecules of non-condensable permanent gases such as CO and CO_2. The remaining solid residue is known as charcoal having higher calorific value about 32 MJ/kg [13] than bio mass and bio oil, easy to transport, store and distribute and more efficient in burning and has a characteristic feature of creating less pollution. It is primarily carbon (~85%), but it can also contain some oxygen and hydrogen. The char can be used as an adsorbent in waste water treatment. The volatiles produced during the primary decomposition of biomass contain both condensable gases (vapor) and non-condensable gases (primary gas). Heavier molecules of the volatiles condense upon cooling, adding to the liquid yield of pyrolysis. The non-condensable gas mixture contains lower-molecular-weight gases like carbon dioxide, carbon monoxide, methane, ethane, and ethylene which do not condense on cooling. The non-condensable gases produced through secondary cracking of the vapor are called secondary gases. The final non-condensable gas product is thus a mixture of both primary and secondary gases. The LHV of primary gases is typically 11 MJ/Nm^3, but that of pyrolytic gases formed after severe secondary cracking of the vapor is much higher: 20 MJ/Nm^3 [11].

2.7 FACTORS AFFECTING PYROLYTIC LIQUID YIELD

The yield of liquid product depends upon the following factors: [14]

- Design of pyrolyzer
- Physical and chemical properties of biomass

- Heating rate
- Final temperature (pyrolysis temperature)
- Residence time in the reaction zone
- Pressure
- Ambient gas composition
- Presence of mineral catalysts

By changing the final temperature and the heating rate, it is possible to change the relative yields of the solid, liquid, and gaseous products of pyrolysis. Rapid heating yields higher volatiles and more reactive char than produced by a slower heating process; slower heating rate and longer residence time result in secondary char produced from a reaction between the primary char and the volatiles.

2.8 TYPES OF PYROLYSIS

The process pyrolysis occurs in three different ways, namely fast pyrolysis, slow pyrolysis and flash pyrolysis.

2.8.1 Fast pyrolysis

In fast pyrolysis process the feed stock is rapidly heated (high rate of heating) in absence of oxygen at high temperature. During the decomposition, biomass generates vapors, aerosols, and some charcoal-like char. After cooling and condensation of the vapors and aerosols, a dark brown mobile liquid is formed that has a heating value that is about half that of conventional fuel oil. Fast pyrolysis is a more advanced process that can be carefully controlled to give high yields of desired liquid products.[15][16][17] Fast pyrolysis process produces 60-75 wt % of liquid bio-oil, 15-25 wt % of solid char, and 10-20 wt % of non-condensable gases, depending on the feedstock used. No waste is generated, because the bio-oil and solid char can each be used as a

fuel and the gas can be recycled back into the process. [16] Fast pyrolysis of rape seed was carried out by Onay et al. in a well-swept fixed bed reactor and reported that the maximum yield is 68% at pyrolysis temperature of 550^{o}C with particle size 0.6–0.85mm, heating rate of 300^{o}C/min and N_2 flow rate of 100cm^3/min. [18] Fast pyrolysis of rape seed was also done by Kockar et al. and investigated effect of temperature, heating rate, particle size, and sweep gas flow on the product yield and concluded that, the yield of char decreases to 14.5% from 27% with increasing in temperature and maximum 73% yield of oil at a temperature of 550–600^{o}C, particle size of +0.6–1.25 mm, and sweep gas flow rate of 100 cm^3/min. [19] Fixed-bed fast pyrolysis experiments have been conducted on cottonseed cake by Nurgu et al. to determine the effects of pyrolysis temperature, heating rate and sweep gas flow rate on pyrolysis yields of the product oil and concluded that the maximum oil yield of 34.8% final temperature of 550^{o}C with a heating rate of 700^{o}C/min and nitrogen flow rate of 100cm^3/ min. [20]

2.8.2 Slow pyrolysis

Slow pyrolysis is also known as conventional pyrolysis. When pyrolysis is carried out at slow heating rate (3-7K/min), it is known as slow pyrolysis. Several literatures reveal that in case of slow pyrolysis, the yield of oil is less and char yield is more. [16][17] Conventional pyrolysis involves all three types of pyrolysis product (gas, liquid, and char). As such, it heats the biomass at a moderate rate to a moderate temperature (~600 °C). The product residence time is on the order of minutes. [2] The slow pyrolysis of pomegranate seeds was carried out by Suat Uçar et al. at 400, 500, 600 and 800 °C to know the effect of temperature on the product distribution. The maximum liquid yields were obtained at the temperatures of 500 and 600 °C and the bio-chars produced from pomegranate seeds having carbon rich fuels with high bulk densities and calorific values. [21] H. Beis et al. slowly pyrolysed Safflower seeds in Fixed-bed pyrolyzer to

determine particularly the effects of pyrolysis temperature, heating rate, particle size and sweep gas flow rate on the pyrolytic product yields and their chemical compositions and obtained the maximum oil yield of 44% at temperature of 500°C, particle size range of +0.425–1.25 mm, with heating rate of 5°C/min and sweep gas (N_2) flow rate of 100 cm^3/ min. [22] Safflower (Charthamus tinctorius L.) seed press cake was pyrolyzed in a fixed-bed reactor from temperature 400-600^oC at different heating rate (10, 30, 50^oC/min) under the sweep gas of N_2 with a flow rate of 100 cm^3/min. to investigate the effects of pyrolysis temperature, heating rate and sweep gas flow rates on the yields of the products by Sensoz et al. and obtained the maximum yield of bio-oil 36% by weight at 500^oC with a heating rate of 50^oC/ min under the sweep gas of N_2 with a flow rate of 100 cm^3/min. due to the decrease in mass transfer limitations. [23] Sensoz et al. studied the Pyrolysis behavior of cotton-seed cake under clinoptilolite catalyst at different conditions and investigated the effect of pyrolysis temperature, catalyst and sweeping gas flow rate and concluded that maximum 30.84% of liquid yield at temperature of 550^oC, sweeping gas flow rate of 100 cm^3 /min in the presence of clinoptilolite catalyst (20% based on raw material) [24] Rapeseed cake was pyrolyzed by Filiz Karaosmanogi et al. in a fixed bed stainless steel reactor from temperature 450-850°C under static atmosphere at rates of 15°C/min and 25°C/min towards understanding the influence of heating rate and pyrolysis temperature on product yield. The maximum yield was obtained at 650°C at a heating rate of 15°C/ min. [25] Pyrolysis experiments on soybean cake was carried out by E. Putun et al. in a fixed-bed reactor under nitrogen and steam atmosphere and obtained the maximum yield of oil 33.78% at 550^oC of particle size 0.850>*D*p<1.250 mm when sweeping gas (N_2) flow rate was 200 cm3/min and the oil yield increased to 42.79% with a steam velocity of 1.3 cm/s. [26] The gas products obtained from the pyrolysis of rapeseed oil cake carried out by Suat Ucar et al. in a

fixed bed reactor at 500°C, mainly consisted of CO_2, CO, CH_4 and H_2S gas and liquid contains oleic acid, 1H-indole, 2,3,5-trimethoxy toluene, toluene, (Z)-9-octadecanamide, psoralene, phenol and phenol derivatives. The water phase contains both non-aromatic and aromatic hydrocarbon compounds and gave the conclusion that the calorific value of the liquid was nearly same at all temperature. [27] S. Sensoz et al. investigated the effect of particle size on the yields of the pyrolysis products of Brassica napus L. in a Heinze reactor under static atmosphere at a temperature of 500°C at 40°C/min of heating rate with a particle size of range of 0.224-1.8 mm, maximum 46 wt% oil obtained with a particle size range of 0.85-1.8 mm with a heating value of 38.4 MJ/kg. [28] Rapeseed Pyrolysis were performed by Ozlem Onay et al. in a free fall reactor at atmospheric pressure under nitrogen atmosphere to investigate the effect of final pyrolysis temperature, particle size and sweep gas flow rate on the yields of products and resulted that the maximum pyrolysis conversion of 7.8% at a temperature of 700°C. The maximum bio-oil yield of 75% was obtained at a final pyrolysis temperature of 600°C, particle size range of 0.224 to 0.6 mm and the sweep gas flow rate of 100 cm^3/ min. [29] Ayse et al. studied Rapid and slow pyrolysis of pistachio shell and concluded that the highest bio-oil yield with a value of 27.7% At a temperature of 773 K. when the heating rate and carrier gas flow rate were as 300 K/min and 100 cm^3/ min respectively. [30]

2.8.3 Flash Pyrolysis

In case of flash pyrolysis biomass is heated rapidly in the absence of oxygen to a relatively modest temperature range of 450 to 600 °C where the reaction time is 30 to 1500 ms [14]. Upon cooling, the condensable vapor is then condensed into a liquid fuel known as bio-oil. Such an operation increases the liquid yield while reducing the char production. A typical yield of bio-oil in flash pyrolysis is 70 to 75% of the total pyrolysis product. There are three types of flash

pyrolysis such as flash hydro-pyrolysis, rapid thermal process, solar flash pyrolysis and vacuum flash pyrolysis.

(a) Flash hydro-pyrolysis:

Hydro-pyrolysis is one type of flash pyrolysis done in hydrogen atmosphere. It is carried out at a pressure up to 20Mpa [31].

(b) Rapid thermal process:

It is a particular heat transfer process with very short heat residence times (between 30 ms and 1.5 s). It is done at temperatures between 400 and 950^{o}C. Rapid de-polymerization and cracking of feed stocks takes place. Rapid heating eliminates the side reactions whereby giving products with comparable viscosity to diesel oil [32].

(c) Solar flash pyrolysis:

Concentrated solar radiation can be used to perform flash pyrolysis. The solar energy can be obtained through devices like solar towers, dish connectors, solar furnaces, etc. Jaques Lede and Oliver Bouten (1999) reported solar flash pyrolysis of samples of cellulose [33].

(d) Vacuum flash pyrolysis:

In this process, pyrolysis is done under vacuum. It limits the secondary decomposition reactions, which in turn gives high oil yield and low gas yield. The vacuum facilitates the removal of the condensable products from the hot reaction zone. This prevents further cracking and further re-condensation reactions. Roy et al. (1999, Canada) reported vacuum pyrolysis of carboniferous age oil shell [34]. Many researchers have used flash pyrolysis process to increase the liquid and the gaseous products

2.9 COMPOSITION OF PYROLYTIC PRODUCTS

2.9.1 Composition of pyrolytic oil

The oil obtained from pyrolysis of bio mass contains several types of organic and inorganic compounds are mentioned below:

1. Acids: Formic, acetic, propanoic, hexanoic, benzoic, etc.
2. Esters: Methyl formate, methyl propionate, butyrolactone, methyl n-butyrate, velerolactone, etc.
3. Alcohols: Methanol, ethanol, 2-propene-1-ol, isobutanol, etc.
4. Ketones: Acetone, 2-butanone, 2-butanone, 2-pentanone, 2-cyclopentanone, 2,3 pentenedione, 2-hexanone, cyclo-hexanone, etc.
5. Aldehydes: Formaldehyde, acetaldehyde, 2-butenal, pentanal, ethanedial, etc.
6. Phenols: Phenol, methyl substituted phenols.
7. Alkenes: 2-methyl propene, dimethylcyclopentene, alpha-pinene, etc., Aromatics:
8. Benzene, toluene, xylenes, nphthalenes, phenanthrene, fluoranthrene, chrysene, etc.
9. Nitrogen compounds: Ammonia, methylamine, pyridine, methylpyridine, etc.
10. Furans: Furan, 2-methyl furan, 2-furanone, furfural, furfural alcohol, etc
11. Guaiacols: 2-methoxy phenol, 4-methyl guaiacol, ethyl guaiacol, eugenol, etc.
12. Syringols: Methyl syringol, 4-ethyl syringol, propyl syringol, etc
13. Sugars: Levoglucosan, glucose, fructose, D-xylose, D-arabinose, etc.
14. Miscellaneous oxygenates: Hydroxyacetaldehyde, hydroxyacetone, dimethyl acetal, acetal, methyl cyclopentenolone, etc. [3]

The inorganic species present in bio oil are in the following forms:

(i) Associated with counter ions.

(ii) Connected to organic acids.

(iii) Related to various enzymatic compounds.

Inorganics present in the bio oil comprises of Ca, Si, K, Fe, Al, Na, S, P Mg, Ni, Cr, Zn, Li, Ti, Mn, Ln, Ba, V, Cl, etc. [3]

2.9.2 Composition of pyrolytic gases

Pyrolysis gas comprises of CO, CO_2 and CH_4. The other components present are H_2, propane, propylene, butane, butenes, C_5, ethane, etc.

2.9.3 Composition of pyrolytic char

Char contains elemental carbon along with hydrogen. In addition, char also comprises of various inorganic species.

2.10 APPLICATION OF PYROLYSIS PRODUCTS

The application of the common products (pyrolysis oil, pyrolysis char and pyrolysis gas) obtained from pyrolysis of biomass is given below:

2.10.1 Application of pyrolysis oil

The bio-oil obtained from pyrolysis can have the following industrial applications:

- combustion fuel
- used for power generation
- production of chemicals and resins
- can be used as a transportation fuel and could be a good substitute for fossil fuels
- can be used as liquid smoke
- production of anhydride-sugars like laevoglucose

- used as binders for palletizing and briquetting of combustible organic waste materials
- bio-oil can be used as preservatives, e.g. wood preservative
- a suitable blend of a pyrolysis liquid with the diesel oil may be used as diesel engine fuel
- bio-oils can be used in making adhesives
- the oil obtained from sewage sludge pyrolysis can be used directly in diesel fuelled engines
- the oil may be stored and transported, and hence need not to be used at the production site

2.10.2 Application of gas

Pyrolysis gas containing significant amount of carbon dioxide along with methane, might be used as a fuel for industrial combustion purposes.

2.10.3 Application of char

The char can be utilized for various industrial usages which are discussed as follows [35]:

- The char could be used as a solid fuel in boilers. The char can be converted into briquettes alone or mixed with biomass and can be used as high efficiency fuel in boilers.
- The char could be used for the production of activated carbon.
- Possibility of using this carbon feedstock for making carbon-nano-tubes may be explored.
- It can be used further for the gasification process to obtain hydrogen rich gas by thermal cracking.

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CHAPTER-3

(EXPERIMENTAL SECTION)

3. EXPERIMENTAL SECTION

3.1 Methodology

Experiments were carried out on different bio mass samples, mainly on oil containing seeds in order to study and fulfill the objective of the project. Different seed samples like castor, soybean seed and polanga de-oiled cake are pyrolyzed in a semi batch reactor. The TGA of the raw materials were carried out to know the degradation temperature. The liquid product obtained is characterized according to their physical properties and elemental composition. EDX of the liquid samples were conducted to investigate the elemental composition. The functional group has been identified using Fourier Transform Infrared Spectroscopy (FTIR) and chemical analysis using GC-MS analyzer. The fuel properties like flash point, fire point, pour point and calorific value were characterized. The char residue remaining in the reactor is subjected to SEM/EDX analysis to know the pore structure and elemental composition.

3.2 Raw materials

The raw materials are castor seed (Fig.3.1), soybean seed (Fig.3.2) and polanga de-oiled cake (Fig.3.3). The seeds are crushed into small sizes and dried in an oven at a temperature of 105^{o}C and used as feed.

Fig. 3.1 Castor seed

Fig. 3.2 Soybean seed

Fig. 3.3 Polanga seed de-oiled cake

3.3 Thermal properties of raw materials using TGA

The thermo gravimetric analysis (TGA) of raw materials was done using the DTG 60 instrument. The apparatus uses a horizontal differential system balance mechanism. 6-8 mg of samples was taken for each analysis. Samples were placed in a platinum container. TGA was carried out at heating rate of 20^{o}C/min. in presence of atmospheric air. The samples were heated up to final temperature of 700^{o}C. The thermo gravimetric weight loss curve (TG, Wt %) were recorded as a function of temperature. The TGA analysis of the samples such as castor seed, soybean seed, polanga de-oiled cake were analyzed. The TGA analysis of different samples depends on the amount of cellulose, hemicelluloses and lignin content of that sample.

3.4 Characterization of raw materials

The raw materials were characterized according to their proximate and ultimate analysis.

3.4.1 Proximate analysis

Proximate analysis gives the idea about the % of moisture, volatile, ash and fixed carbon content in the respective samples.

i. Determination of moisture content

One gram of air dried sample was taken in a crucible and kept in an electrically heated oven at a temperature of 105^{o}C for one hour. After one hour the sample was taken out and cooled in desiccators. The percentage loss of weight gave the percentage of moisture in the sample.

Percentage of moisture content= loss in weight * 100/ wt. of sample taken

ii. Determination of volatile matter

The dried samples after moisture removal was then taken in a crucible and placed in an electrically heated furnace at a temperature of 925^{o}C for seven minutes and then cooled in desiccators. The percentage of weight loss gave the volatile matter content.

Percentage of volatile matter = loss due to removal of volatile matter*100/ wt. of sample taken

iii. Determination of ash content

The remaining sample after determination of volatile matter was kept in furnace at a temperature of 600-700^{o}C for one and half hour. The percentage of weight loss gave the ash content.

Percentage of ash = weight of ash left*100/ wt. of sample taken

iv. Determination of fixed carbon

Percentage of fixed carbon = 100- % of (moisture +volatile+ ash) content

3.4.2 Ultimate analysis

The ultimate analysis was carried out in CHNSO elemental analyzer (Vario El Cube Germany) to know the elemental composition.

3.5 Experimental set up

Fig. 3.4 shows the schematic diagram of the biomass pyrolysis experimental set up and Fig. 3.5, the experimental set up. The pyrolysis unit consists of pyrolysis reactor, electrically heated furnace, PID controller, glass condenser and measuring cylinder. The temperature of the furnace was maintained by highly sensitive PID controller.

Fig. 3.4 Schematic diagram of experimental set up

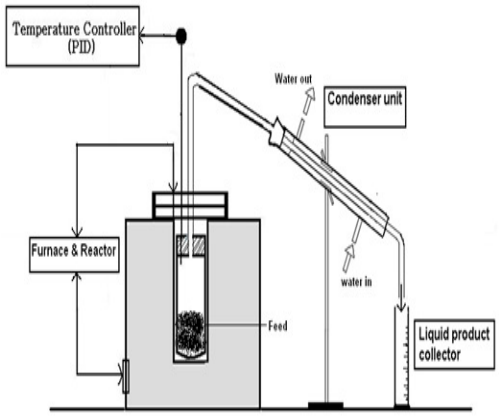


Fig. 3.5 Experimental set up

3.6 Reactor specification

The reactor (Fig. 3.6) is cylindrical shaped vessel made up of stainless steel having capacity of ½ liter. The pyrolysis experiments were performed in an apparatus designed with a batch reactor of height 16.5cm, 4.7 cm ID and OD 5.0 cm. in diameter.

Fig. 3.6 Reactor

3.7 Experimental procedure

The seed raw materials were purchased from the market and used directly as feed to the reactor. A series of experiments were conducted to determine the influence of temperature between 450-600^{o}C at a rate of 20^{o}C/ min. The pyrolysis experiments were performed in a semi batch reactor, inserted vertically into an electrically heated furnace. The temperature is controlled by a PID controller. 15 gm of castor seed, polanga de-oiled cake and 20 gm of soybean as feed was pyrolyzed at each run and the vapor generated from the reactor was condensed in a water cooled condenser. The condensed liquid was collected in a measuring cylinder as liquid and separated into two fractions (aqueous and fuel) by gravity separation as shown in Fig. 3.7. The residue char in the reactor (Fig. 3.8-3.10) was collected after cooling the reactor.

Fig. 3.7 Gravity separation of pyrolytic oil

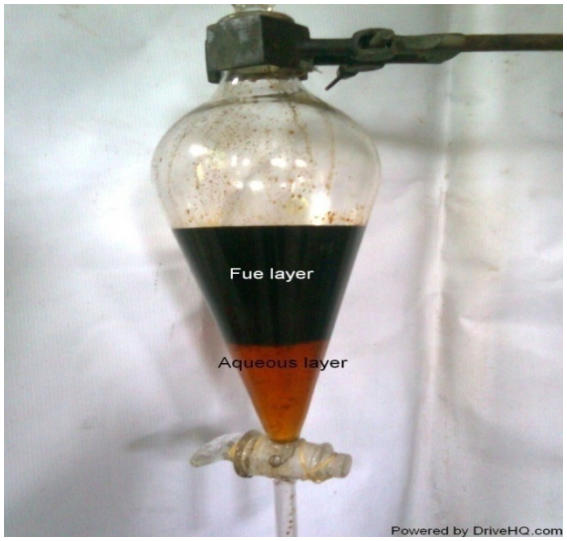


Fig. 3.8 Castor seed char

Fig. 3.9 Polanga de-oiled cake chars

Fig. 3.10 Soybean seed char

Fig. 3.11-3.13 shows the photo graph of pyrolytic oil obtained from castor seed, polanga seed, soybean seed and polanga seed de-oiled cake.

Fig.3.11 Castor seed pyrolytic oil

Fig.3.12 Soybean seed pyrolytic oil

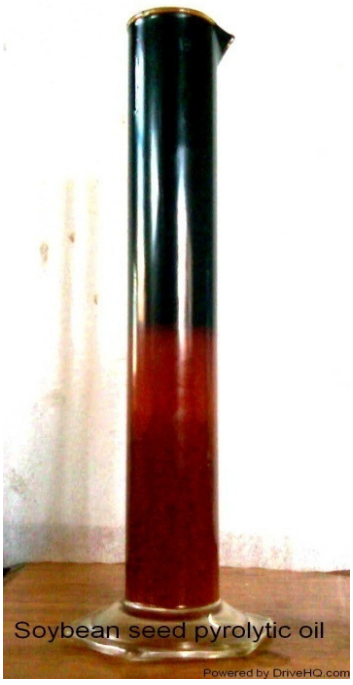


Fig.3.13 Polanga seed de-oiled cake pyrolytic oil

3.8 Characterization of pyrolytic oil

The pyrolytic oils obtained were characterized for their physical and chemical properties. The physical properties such as viscosity, density, calorific value, pH, flash point, fire point, pour point, color of all pyrolytic oil were determined and mentioned in the result and discussion part. The pH of the samples was determined using the pH meter EUTECH pH 510. The calorific value was measured using bomb calorimeter and flash point and pour point by flash point apparatus and pour point apparatus.

3.9 Determination of functional group of pyrolytic oil

Fourier Transform Infrared spectroscopy (FTIR) of all pyrolytic oils obtained at temperature of 550^{o}C were analyzed in a Perkin-Elmer infrared spectrometer with a resolution of 4cm^{-1} and in the range of 400- 4000cm^{-1} to know the functional group present.

3.10 Elemental analysis of pyrolytic oil

EDX analysis of pyrolytic oil was carried out by EDX analyzer (JEOL, JSM-6480LV equipped with a 6587 scanning spectrometry detector) to know the weight percent of elements present with the concentration and atomic weight.

3.11 GC-MS analysis of pyyrolytic oil

The chemical compound present in the pyrolytic oil was analyzed using GC-MS-OP 2010[SHIMADZU] analyzer.

3.12 Characterization of pyrolytic char

The pyrolytic char was characterized according to their calorific value, pore structure, and elemental analysis. The calorific value was measured using bomb calorimeter and SEM/EDX for pore structure and elemental analysis.

CHAPTER-4

(RESULTS AND DISCUSSION)

4. RESULTS AND DISCUSSION

4.1 Characterization of raw materials

Proximate and ultimate analysis was used to characterize the raw materials. The proximate analysis determines the Moisture, volatile matter, Ash, fixed carbon content in the fuel. It is a quick and practical way of assessing the fuels quality and type. The moisture content of biomass has a marked effect on the conversion efficiency and heating value. Higher moisture of biomass has a more tendency to decompose resulting in energy loss during storage. Volatile matter evolves in the form of gas, light, hydrocarbon and tars. Volatile matter of the biomass is higher than the coal (around 75%). Higher volatile matter of the biomass makes it more readily de-volatilized than solid fuel. Liberating less fixed carbon hence makes them more useful for pyrolysis and gasification. Ash content and moisture content affect the heating value. The ash content in the bio mass is an integral part of plant structure which consists of a wide range of mineral matter such as salt of calcium, potassium, silica and magnesium. Ash content depends upon the plant and soil condition in which the plant grows. The proximate and ultimate analysis of all raw materials are given in Table 4.1 and Table 4.2 respectively which shows that the raw materials contains higher percentage of volatile matter and less amount of moisture and ash content and higher weight percentage of oxygen followed by carbon and hydrogen with a fewer amount of sulphur.

Table 4.1 Proximate analysis of raw materials

Raw materials	Moisture content (%)	Volatile matter (%)	Ash content (%)	Fixed carbon (%)
Castor seed	27.37	61.29	9.14	2.2
Soybean seed	7.94	72.28	6.07	13.71
Polanga de-oiled cake	0.34	73.49	2.08	24.09

Table 4.2 Ultimate analysis of raw materials

Raw materials	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)	Sulphur (%)	C/N ratio	C/H ratio
Castor seed	59.288	6.167	2.45	30.095	0.03	24.119	9.6137
Soybean seed	48.37	7.476	6.36	37.449	0.345	7.6.29	6.4701
Polanga de-oiled cake	42.22	6.7	3.35	46.915	0.815	12.605	6.3025

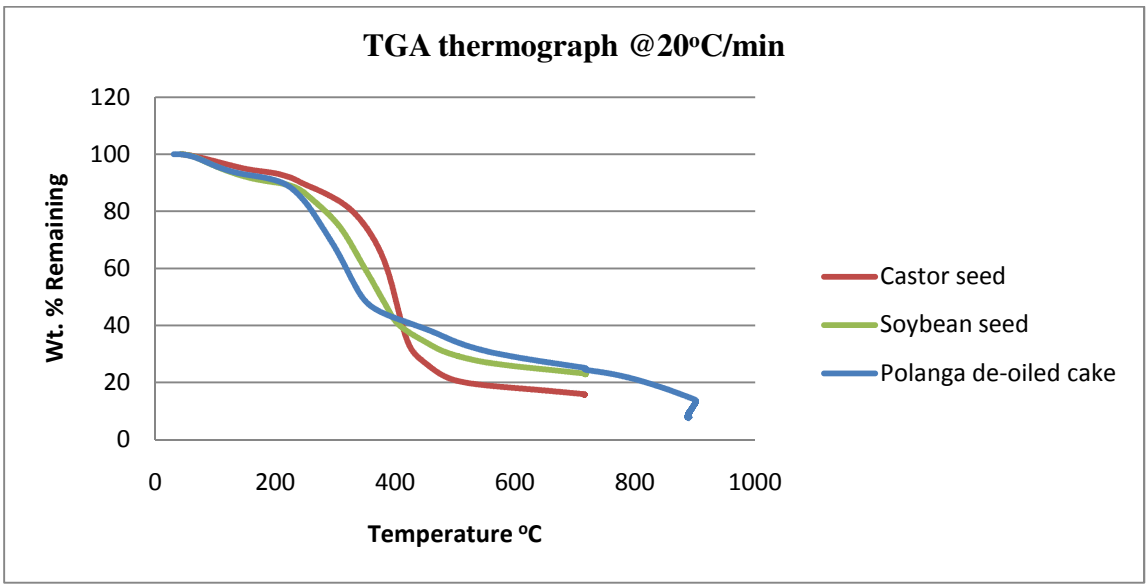
4.2 Thermo gravimetric analysis of raw materials (TGA)

The TGA thermograph of castor seed, soybean seed and polanga de-oiled cake at a heating rate of 20^{o}C/min under air atmosphere are shown in Fig. 4.1. The characteristic parameters of de-volatilization are presented in this section. A three stage weight loss was observed. The initial decomposition or 1st. decomposition occurred between 35 to 200^{o}C for soybean and castor seed. That represents 4.99 %, 6.71% weight loss at the heating rate of 20^{o}C/ min for soybean and castor seed respectively. The rapid decomposition, the 2nd decomposition of the sample occurred between 200 to 500^{o}C representing an 70.41%, weight loss for soybean and 79.24% for castor seed and remaining 22.88%, 15.77% of residue for soybean and castor seeds respectively. The 1$^{st.}$ stage decomposition represents the evaporation of moisture contents, 2$^{nd.}$ decomposition indicates the formation of volatiles mainly. During the 3rd stage, the pyrolysis residue slowly decomposed, with the weight-loss velocity becoming smaller and smaller and the residue ratio tends to be constant at the end the decomposition of hydrocarbon. But in case of polanga de-oiled cake only two stage of decomposition was visible, that means after initial decomposition (up to 200^{o}C) the secondary decomposition (700^{o}C) continued up to the final temperature.

Due to high decomposition rate, the rapid decomposition zone or 2nd stage of decomposition is treated as active pyrolytic zone. During the 2nd stage, the intermolecular associations and weaker

chemical bonds are destroyed. The side aliphatic chains may be broken and some small gaseous molecules are produced because of the lower temperature. During the 3rd stage with higher temperature chemical bonds are broken and the parent molecular skeletons are destroyed. As a result, the larger molecule decomposes to smaller molecules in the form of gas phase. Finally coke remains. [1-5]

Fig. 4.1 TGA thermograph of raw materials



4.3 Influence of temperature on product yield

Fig. 4.2 shows the product yield at a heating rate of 20°C/ min for slow pyrolysis of castor seed. It was observed that the yield of liquid product increases with increase in temperature. But up to a certain temperature (550°C), the liquid increases and then decreases with increase in temperature due to the formation of more amounts of non condensable gases/volatiles. As the temperature increases the char yield decreased because of the secondary reaction taking place at the third stage of pyrolysis, which means the char materials decomposes at higher temperature. In case of castor seed pyrolysis, the liquid yield increases from 46.66 to 66.66% by volume observed from fig. 4.2 and 50.6 to 64.40% by weight as the final temperature raised from 475-

550°C at the same time char yield decreases from 22.53 to 20.93%. After temperature 550°C, when pyrolysis temperature increased to 600°C the density of oil increased means the weight of oil was more with the same volume oil. It may be due to the formation of denser products at high temperature and lower residence time of feed materials in the reactor. Fig. 4.5 shows the effect of temperature on completion time. Both yield of liquid and completion time of pyrolysis is a function of temperature. So, 550°C is the appropriate temperature for pyrolysis of castor seed to get maximum yield of oil with low density and less completion time. [6-17]

Fig. 4.2 Influence of temperature on slow pyrolysis of castor seed

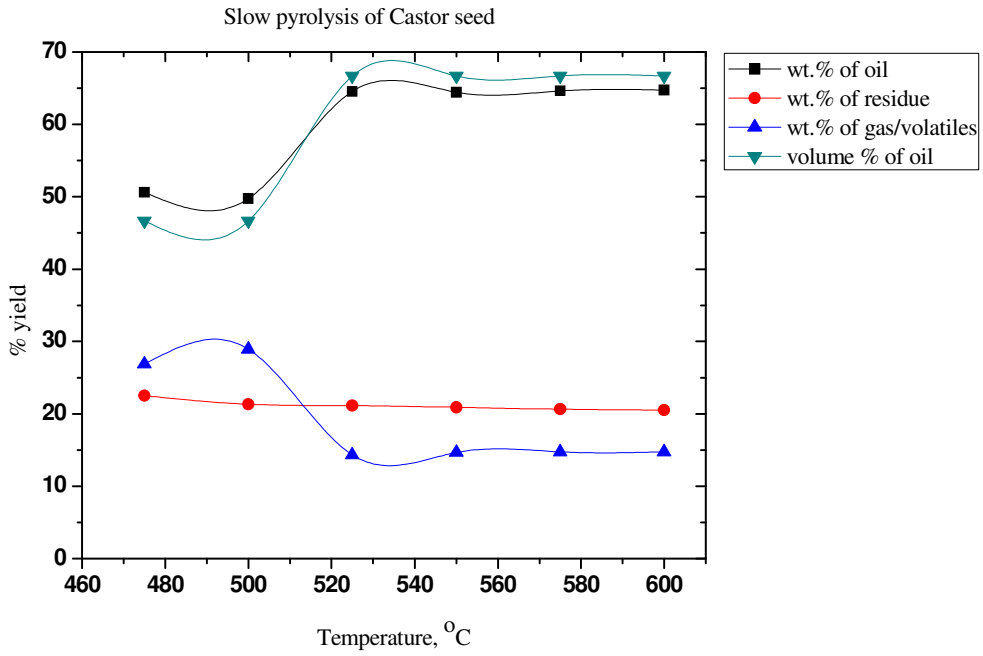


Fig. 4.3 shows the yield of products from slow pyrolysis of soybean seed. The liquid yield increases from 44.1% to 59% by weight and 40% to 54.25% by volume as the temperature increases from 450 to 550°C and then decreases as temperature raised to 600°C due to generation of non condensable gases. Here the conversion was also maximum 77.3% at 550°C, with a 22.7% of remaining char the reactor. From fig. 4.3 and fig. 4.5, observed that pyrolysis of

soybean seed yields maximum liquid on volume basis was equal in the temperature between 525 to 600°C with an equal duration.

Fig. 4.3 Influence of temperature on slow pyrolysis of Soybean seed

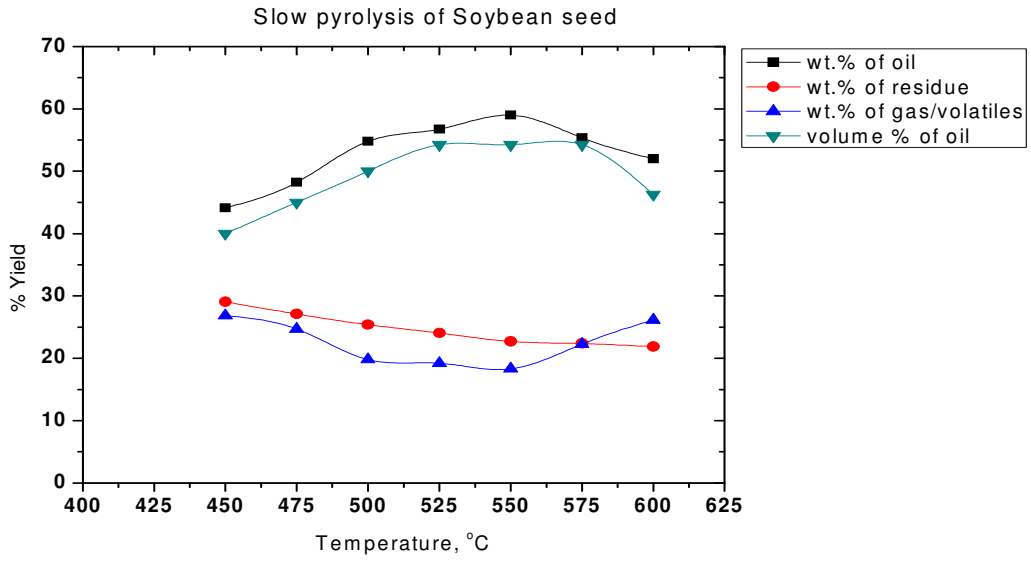


Fig. 4.4 shows the yield of products from slow pyrolysis of polanga de-oiled cake. The effects of temperature also have the same effect as described above in case of castor and soybean seed. The volumetric yield of liquid was equal from temperature of 500 – 575°C, and the weight of liquid was equal at 500 and 525°C and then increased with the temperature. But at a temperature of 550°C the volumetric yield was maximum at a less completion time (Fig. 4.5). So in this case also 550°C is the optimum temperature to get maximum yield of oil.

Fig. 4.4 Influence of temperature on slow pyrolysis of Polanga de-oiled cake

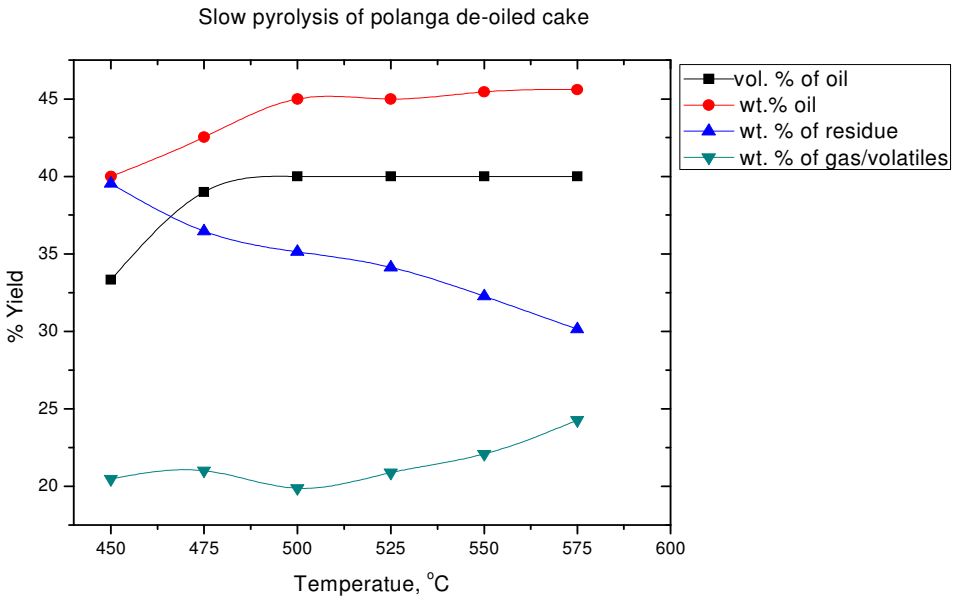
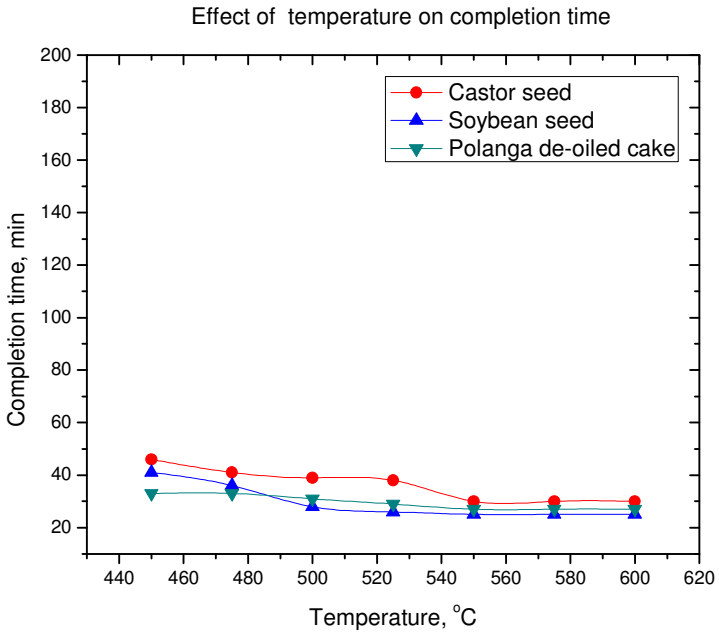


Fig. 4.5 shows the effect of temperature on completion time. It was observed that the temperature has a positive effect on completion time. The completion time decreases with increasing the pyrolysis temperature. This may due to the formation of more amounts of volatiles within a short duration of time. [6-17] The optimum temperature for production of pyrolytic oil can be obtained by comparing the volumetric yield of pyrolytic oil, completion time of pyrolysis with pyrolysis temperature.

Fig. 4.5 Influence of temperature on completion time



4.4 Fractionation of pyrolytic oil

The pyrolytic oil can be easily separated into two fractions by gravity separation process as shown in Fig. 3.7. The upper layer is known as fuel layer and bottom layer is the aqueous layer. Basically the upper part can be used as alternative to fuel and the bottom layer is a mixture of water and some fractions of organic liquids mostly carbohydrate derived compounds. The fuel properties of the top layer are given in Table 4.3. The aqueous extract of bio oil includes both low molecular weight aldehydes that are effective meat browning agent (especially glycol aldehyde) as well as phenolic compounds that provide a smoky flavors. A potential application of the water soluble fraction of bio oil is the production of salt of calcium carboxylic acid that can be used as ecofriendly road de-icers. The water insoluble fraction that usually constitutes 25-30% of the whole bio-oil is often called pyrolytic lignin because it is essentially composed of oligomeric fragments originating from degradation of native lignin. [18]

So the pyrolytic oil obtained from pyrolysis of castor seed and polanga de-oiled cake is valuable from fuel and chemical point of view. (Table 4.3, 4.6, 4.7)

4.5 Characterization of pyrolytic oil

Characterization of pyrolytic oil obtained by the slow pyrolysis of castor, soybean seeds and polanga de-oiled cake were characterized according to their physical/fuel properties as described in the experimental section. The physical properties of fuel layer are given here. Table 4.3 shows the optimum temperature of pyrolysis to get maximum volumetric yield and the comparison between castor and polanga de-oiled cake pyrolytic oil with diesel. The colour and odour of all pyrolytic oil was dark reddish brown and a distinctive smoky smell. All pyrolytic oil was separated into two layers, fuel layer and aqueous layer. All physical properties like flash point, fire point, density, viscosity and calorific value are comparable with diesel. The pyrolytic oils are soluble with petroleum products like petrol, diesel, toluene and methanol; also the calorific values are very near to diesel. So the pyrolytic oil is comparable with diesel and can be used with addition to diesel in transportation purpose. The CHNO analysis of the pyrolytic oil shows that the pyrolytic oil contains maximum amount of C, H and O. Higher the C/H ratio shows the oil having good calorific value, can be observed from the Table 4.3.

Table 4.3 Physical properties of different pyrolytic oil and diesel

Physical properties of castor seed, polanga de-oiled cake pyrolytic oil at the optimum temperature (maximum liquid yield)			
Pyrolytic oil	Castor seed pyrolytic oil	Polanga de-oiled cake pyrolytic oil	Diesel
Maximum volumetric yield	66.66%	40%	--
Optimum temperature for maximum yield	550^{o}C	500^{o}C	--
Appearance	Typically a dark brown free flowing liquid	Typically a dark brown free flowing liquid	Yellowish
Odour	A distinctive smoky smell	A distinctive smoky smell	Aromatic
Calorific value	8527.5 Kcal/Kg	9635 Kcal/Kg	10700Kcal/Kg
Flash point	31^{o}C	43^{o}C	76^{o}C
Fire point	35^{o}C	46^{o}C	-
Pour point	<5^{o}C	16.5^{o}C	-16^{o}C
Density	0.966@ 30^{o}C gm/cc	1.133 @30^{o}C gm/cc	0.85 gm/cc
Viscosity	8.32CST @40^{o}C	14.3CST@40^{o}C	2.5 CST
pH	3.7	4.1	-
Miscibility	Methanol, Ethanol, Toluene, Diesel and petrol	Methanol, Ethanol, Toluene, Diesel and petrol	-
C	59.55 wt.%	71.48 wt.%	
H	10.22 wt.%	9.81 wt.%	
N	6.89 wt.%	7.46 wt.%	
O	23.34 wt.%	11.25 wt.%	
C/H	5.826 wt.%	7.286 wt.%	

4.6 FTIR analysis of pyrolytic oil

The FTIR analysis of the castor, soybean and polanga de-oiled cake pyrolytic oil reveals that the pyrolytic oil having similar functional group (Fig. 4.6). The functional groups present in pyrolytic oil from the FTIR analysis are given in Table 4.4. Broad –OH stretching vibrations in the range of 3600- 3300 cm^{-1} can be the presence of alcoholic and Phenolic in the pyrolytic oil. Those several peaks observed at about 820cm^{-1}-690 cm^{-1} indicates the existence of some substituted groups in the aromatic and Phenolic . The peaks in the range of 1700 cm^{-1}- 1680cm^{1} show the presence of c=o (carbonyl) aldehyde, ketone and ester compound line. The peak between 1575 $cm^{-1}$and 1675 cm^{-1} represents C=C stretching vibration. The peak range between 2930 cm^{-1}-2850 $cm^{-1}$and 1460 cm^{-1}-1377 cm^{-1} shows that the C-H stretching vibration and bending vibration respectively. [16, 19, 20]

Fig. 4.6 FTIR spectra of pyrolytic oil

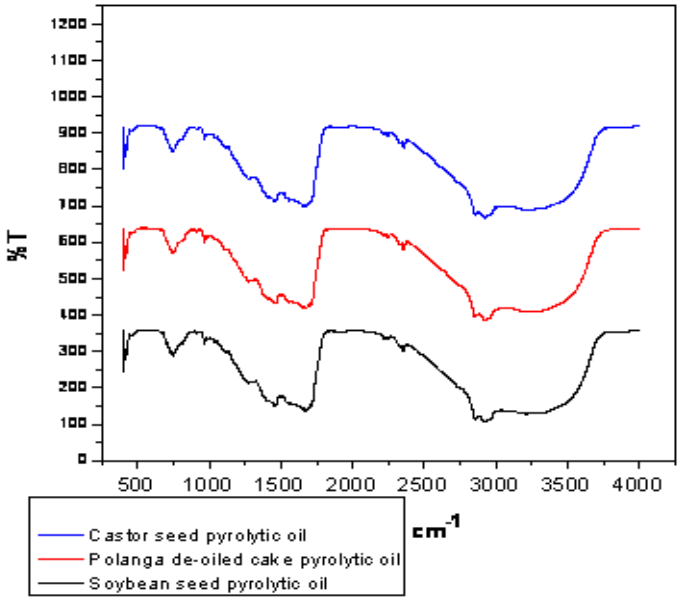


Table 4.4 Functional groups presents in all pyrolytic oil

Functional groups present	Wave number. in cm^{-1}
Broad –OH stretching vibrations, presence of alcohol group	3600- 3300
Aromatic and Phenolic	820-690
C=O (carbonyl) Aldehydes, Ketones and Esters	1700 - 1680
C=C stretching vibration, presence of alkene group	1575-1675
Sp3C-H stretching vibration, presence of alkane group	2930 -2850
C-H bending vibration, CH_2, CH_3 bending vibrations	1460 -1377

4.7 EDX analysis of pyrolytic oil

The elemental analysis of all pyrolytic oils was carried out using EDX analysis. Table 4.5 shows the elemental analysis of pyrolytic oils. Biomass has a higher oxygen content and lower sulphur content than coal. The amount of nitrogen and chlorine present (related to NOx and corrosion) are very significant in bio mass fuel. Biomass also contains more alkaline materials such as potassium and sodium, which is directly linked to the fouling problem. From the elemental analysis, it is observed that the pyrolytic oil contents maximum amount of boron, carbon and oxygen with a minimum amount of Mg, Al, Si, Cl, Cr, Zn and Mn combined with K.

Table 4.5 Elemental analysis of pyrolytic oil

	Soybean seed pyrolytic oil	Polanga de-oiled cake pyrolytic oil	Castor seed pyrolytic oil
Elements	Weight%	Weight%	Weight%
B K	66.67	4.14	28.25
C K	32.56	77.43	69.33
O K	1.77	13.29	2.25
Na K	0	0	0
Mg K	0	0.10	0.02
Al K	0	0.97	0.01
Si K	0	0	0.01
P K	0	0	0
Cl K	0	0.03	0.01
K K	0	0	0
Ca K	0	0	0
V K	0	0	0
Cr K	0	0	0.02
Mn K	0	0.08	0.03
Fe K	0	0.13	0
Zn L	0	0	0.04
As L	0	0	0
Mo L	0	3.30	0.01
Sb L	0	0.81	
S K	0	0.02	

4.8 GC-MS Analysis of pyrolytic oil

The bio-oil characterization was realized by using GC–Mass Spectrometry at the pyrolysis temperatures of 500^{o}C given in Table 4.6- 4.7. The areas of major compounds in bio-oils are given in tables. They were classified with increasing the retention times. Taking into account of area percentage, the highest peak areas of total ion chromatogram (TIC) of compounds were 10-undecenoic acid, Oleic acid, Octadecanonic acid, Octadec-9-enoic acid, N-hexadecanoic acid, 3-phenyl-5-(pyridin-4-ylmethylidene)-2-thioxoimidazolidin-4-one, Z-11-pentadecenal, Oleanitrile, 9-octadecenamide, (z)- Methy; 12-hydroxy-9-octadecenenoate, 2-pentylnon-2-enal, Methy; 12-hydroxy-9-octadecenenoate, 13-hexyl-oxa-cyclotridec-10-en-2-one. Oleic acid (C18H34O2) is a

monounsaturated omega-9 fatty acid found in various animal and vegetable sources. The saturated form of this acid is stearic acid. It is used in Lorenzo's oil. [21]

Second major compound was 1H-indole. Natural jasmine oil, used in the perfume industry, contains around 2.5% of 1H-indole (C_8H_7N). Also, 1H-indole is used in the manufacture of synthetic jasmine oil. Another major compound of bio-oil was psoralene ($C_{11}H_6O_3$). It is the parent compound in a family of natural products known as furocoumarins. An important use of psoralene is in PUVA treatment for skin problems such as psoriasis, eczema and vitiligo. This takes advantage of the high UV absorbance of psoralene. It has also been recommended for treating alopecia [22]

Table 4.6 GC-MS analysis of castor seed pyrolytic oil

CASTOR SEED PYROLYTIC OIL			
Name of the compounds	Area %	Name of the compounds	Area %
2-octanone	1.44	1-dodecanesulfonyl	1.03
Decane	0.41	8-octadecanone	0.35
Oleanitrile	1.04	2-pentadecanone,6,10,14-trymethyl-	0.40
Cyclododecanone	0.52	N-hexadecanoic acid	5.55
2-dodecanone	0.33	13-hexyl-oxa-cyclotridec-10-en-2-one	1.23
Methyl undec-10-enoate	0.70	Oleanitrile	0.90
10-undecenoic acid	26.21	Z-11-pentadecenal	2.71
Undecanonic acid	1.17	3-phenyl-5-(pyridin-4-ylmethylidene)-2-thioxoimidazolidin-4-one	3.84
2-pentylnon-2-enal	1.32	Oleic acid	17.89
8-heptadecene	0.53	Octadec-9-enoic acid	6.29

3-heptadecene,(z)-	0.87	Octadecanonic acid	11.92
Hexadecene	0.59	2-amino-6-n-hepthyl-4-hydroxypteridine	5.24
5-octadeceyne	0.21	Oleanitrile	2.44
1-bromoheptadec-5-ene	0.22	Methy; 12-hydroxy-9-octadecenenoate	1.43
1-cyclododecylethanone	0.29	9-octadecenamide, (z)-	1.65

Table 4.7 GC-MS analysis of polanga cake pyrolytic oil

POLANGA CAKE PYROLYTIC OIL			
NAME OF THE COMPOUNDS	AREA %	NAME OF THE COMPOUNDS	AREA %
Phenol	1.48	pentadecane	1.06
Decane	0.28	1-pentadecene	0.41
2-Methyl phenol	0.57	Hexadecane	0.58
1-Pentyl butane	0.18	8-hepta decene	0.55
p-Hydroxy toluene	1.07	3-heptadecene,-(z)	0.43
2-Methoxy phenol	0.66	1-Nonadecene	0.42
Undecane	0.28	Heptadecane	1.21
2-ethylphenol	0.46	Hexadecanenitrile	2.82
1-hydroxy-d,5-dimethylbenzedn	0.71	Oleic acid	32.89
Pentylbenzene	0.24	Octadec-9-enoic acid	5.68
1-ethyl-4-hydroxybenzene	0.74	Octadecanoic acid	7.68
1-hydroxy-3,5 dimentyhylbenzene	0.28	Octadecanamide	1.65
Ammonim octanoate	0.40	9- Octadecanamide	1.31

1-(2-furranylmethyl)1H-pyrrole	0.12	Octadecanamide	1.48
1-dodecanol	0.19	9,12- octadecadien-1-ol	0.33
1-hydroxy-2-methoxy-4-methyl benzene	0.14	9- Octadecanamide	2.16
Dodecane	0.26	9- Octadecanamide	1.26
o-isopropyl phenol	0.11	Octadecanamide	1.35
4A-methyl-4,4A,5,6,7,8-hexahydro-2(3H)-Napthalenone	0.15	Methyl cis-11,14,17-icosatrienoate: 11,14,17-Icosatrienoic acid, methy ester,(z)	0.68
Benzenepropanenitrile	0.31	3 beta-hydrroxy- 5 beta-Androstan-6, 17 dione	0.69
Tridecane	0.75	Hexadecanoic acid	15.65
4- Cyanobenzoic acid, 6-ethyl-3octyl ester	0.43	Oleanitrile	1.48
Tetradecane	0.63	Oleanitrile	0.92
10-undecenoic acid	0.75		
1-pentadecene	0.35		
Hexadecanoic acid, methyl ester	1.30		

4.9 Characterization of pyrolytic char

Pyrolytic char is characterized according to their calorific values, elemental analysis (EDX) and SEM analysis which are summarized below.

4.9.1 Calorific value

Table 4.9 shows the calorific value of different pyrolytic char obtained from slow pyrolysis of the raw materials taken. The pyrolytic char obtained from castor seed char having higher calorific value about 6922.256 Kcal/kg than soybean seed char (5893.272 Kcal/kg.) and Polanga de-oiled cake char (5168.306 Kcal/kg.). So these chars can be used as solid fuel.

Table 4.8 Calorific values of pyrolytic char

Pyrolytic char	Calorific value, Kcal/kg
Castor seed char	6922.256
Soybean seed char	5893.272
Polanga de-oiled cake char	5168.306

4.9.2 Elemental analysis of pyrolytic char

Table 4.10 shows the elemental analysis of different pyrolytic char obtained from slow pyrolysis of raw materials taken. The elemental analysis shows that the pyrolytic char contains maximum amount of carbon, oxygen, potassium and fewer amounts of magnesium, phosphorous, chlorine, sulfur, calcium, iron, sodium, arsenic and silica. Arsenic is not present in castor seed char and soybean seed char where polanga de-oiled char contains fewer amounts. Si is present only in polanga de-oiled char. Sodium is not present in castor seed char where soybean and polanga de-oiled cake char having fewer amounts. Some amount of calcium is present in castor seed char where other chars do not contain any.

Table 4.9 Elemental analysis of pyrolytic char

	Castor seed char	Soybean seed char	Polanga deoiled cake char
Elements	Weight%	Weight%	Weight%
C	76.82	76.22	61.94
O	14.28	15.85	23.11
Mg	0.32	0.71	0.96
P	2.08	2.11	1.64
S	0.06	0.09	0.3
Cl	0.26	0.11	0.29
K	5.52	5	7.55
Ca	0.37	-	1.59
Fe	0.29	0.08	0.99
As	-	-	0.1
Na	-	0.09	0.06
Si	-	-	1.46

4.9.3 SEM analysis of char

The SEM photo graphs of the char at different magnification are given in fig. 4.7 - 4.16. An important property of pyrolytic char is its morphological similarity with natural carbon. A fundamental use, difference between the commercially sold carbon and the pyrolytic char in the content of inorganic compounds (ZnO, S) as well as SiO_2, Al_2O_3. With increasing in temperature of pyrolysis a reaction between ZnO and S occurs to form ZnS, consisted of individual particles with a density higher than pyrolytic char and the particles can be further separated. Even in this case, the znic content in the pyrolytic char determined by EDX analysis. The character of pyrolytic char with a porous structure is evident from the following photo documentation. So it can be used as an adsorbent as activated carbon.

Fig. 4.7 Castor seed char

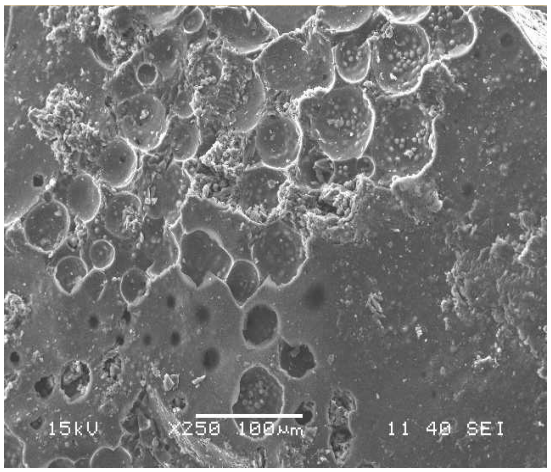


Fig.4.8 Castor seed char

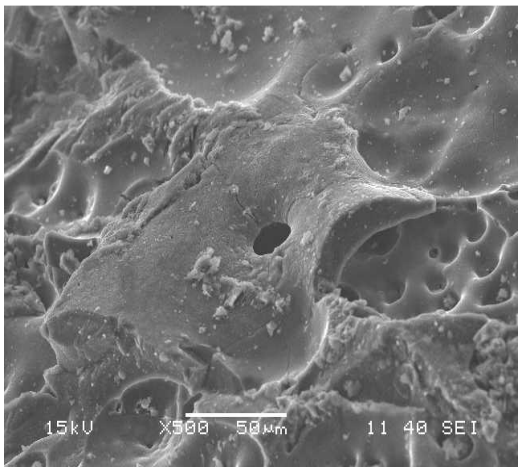


Fig. 4.9 Castor seed char

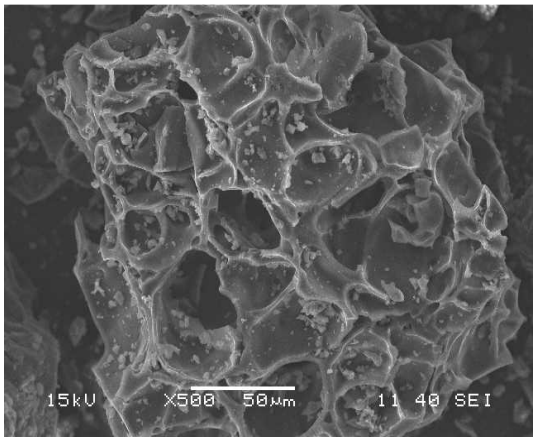


Fig. 4.10 Castor seed char

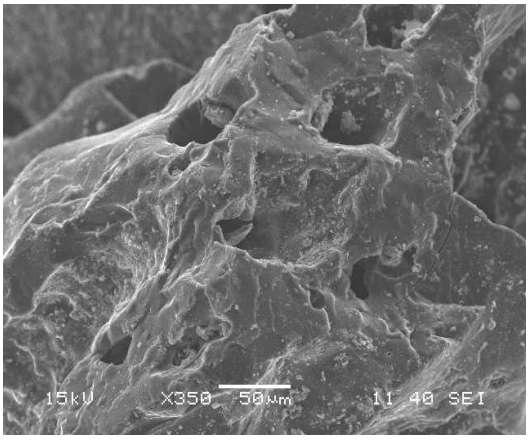


Fig. 4.11 Soybean seed char

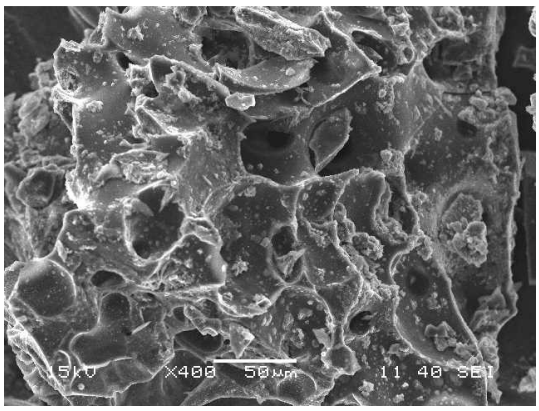


Fig. 4.12 Soybean seed char

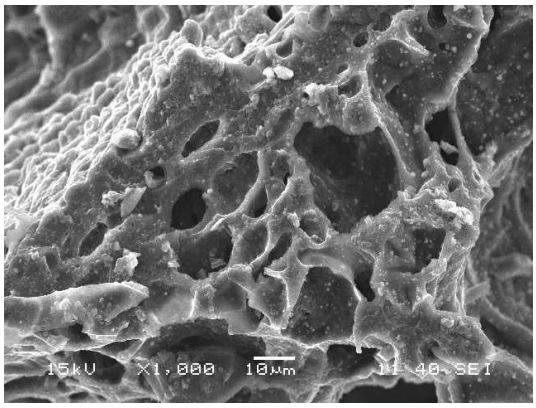


Fig. 4.13 Soybean seed char

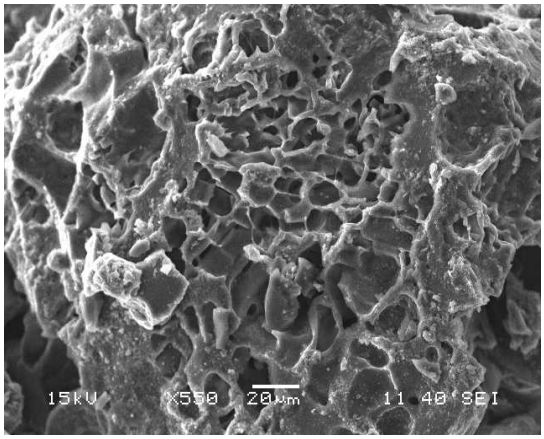


Fig. 4.14 Polanga de-oil cake char

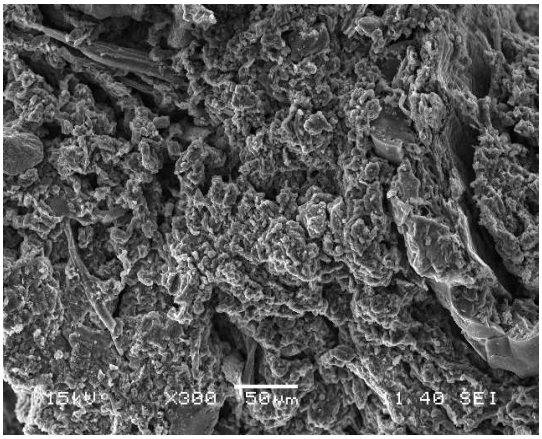


Fig. 4.15 Polanga de-oil cake char

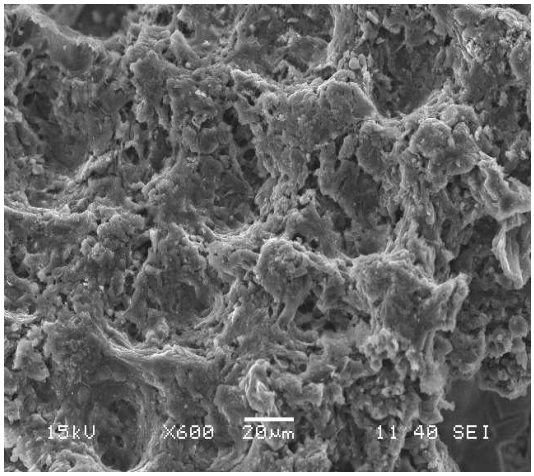
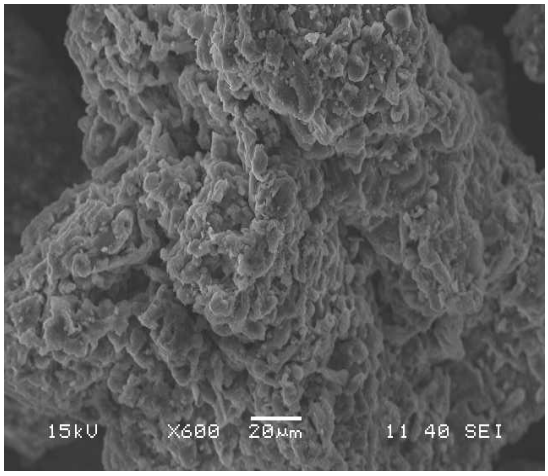


Fig.4.16 Polanga de-oil cake char



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CHAPTER-5

(CONCLUSION)

5 CONCLUSION

Thermal pyrolysis of castor seeds, soybean seeds and polanga de-oiled cake were carried out in a semi batch reactor made up of stainless steel at temperature range from 450^{o}C to 600^{o}C and at a rate of 20^{o}C/min to produce bio-fuel. The maximum yield of oils 66.66%, 54.25% and 40% on volume basis for castor seed, soybean seed and polanga seed de-oiled cake respectively, was obtained at a temperature of 550^{o}C with a less completion time. The pyrolytic oils obtained having similar functional group as other bio-oils given in several literatures. The major compounds present in castor seed pyrolytic oil were 10-undecenoic acid, Oleic acid, Octadecanonic acid, Octadec-9-enoic acid, N-hexadecanoic acid, 3-phenyl-5-(pyridin-4-ylmethylidene)-2-thioxoimidazolidin-4-one, Z-11-pentadecenal, Oleanitrile, 9-octadecenamide, (z)-, Methy; 12-hydroxy-9-octadecenenoate, 2-pentylnon-2-enal, Methyl; 12-hydroxy-9-octadecenenoate, 13-hexyl-oxa-cyclotridec-10-en-2-one with a fewer amounts of ester and alkali compounds. The fuel analysis of oil reveals that these pyrolytic oils can be used as fuel. Due to the unavailability of arsenic compound in the char materials, high calorific value can be used for purification of solvent and solid fuel.

PAPERS COMMUNICATED:

- K.P Shadangi and R.K Singh, "Thermal pyrolysis of oil containing seeds: the effect of temperature on product yields", communicated in energy & fuels.
- R.K Singh and K.P Shadangi, "Thermal Pyrolysis of Castor Seeds to liquid fuels", communicated in Fuel.
- R.K Singh and K.P Shadangi, " Pyrolysis of polanga seed de-oiled cake to produce fuels and chemical feedstocks", communicated in Energy Conversion and Management